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Invited review

Acyl complexes of molybdenum: structural and reactivity studies

Leopoldo Contreras, Antonio Pizzano, Luis Sánchez, Ernesto Carmona *

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales, Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Apdo. 553, 41071 Sevilla, Spain

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Abstract

The following structural peculiarities of the agostic acyl structure $\overline{Mo(C(O)CH_2}R)$ (R=H, $SiMe_3$) and some characteristic chemical reactivity of the M-η^2-acyl and iminoacyl linkage are described. (i) A structural comparison of the bonding parameters within three agostic acetyl Mo complexes containing the dithioacid ligand, indicates that the agostic interaction strengthens upon increasing the electron-releasing properties of the S-chelating ligand. (ii) The acyl-xanthate complex $Mo(C(O)Me)(S_2COR)(CO)(PMe_3)_2$ undergoes loss of a sulfur atom from the coordinated xanthate and coupling with the acyl ligand to form complexes containing coordinated alkoxythiocarbonyl and monothioacetate ligands. The latter can be metathetically replaced by KS_2COR. (iii) Upon heating at 70°C η^2-acyl-dicarbonyl bispirazolilborate complexes of molybdenum of the type $Mo(H_2B(pz^*)_2)(\eta^2\text{-}C(O)Me)(CO)_2(PMe_3)$ (pz^* = 3,5-dimethyl-pyrazol-1-yl) yield functionalized acyl ligands derived from the stereo- and regioselective intramolecular addition of one of the B–H bonds of the $H_2B(pz^*)_2$ group across the C=O moiety of the η^2-acyl group. (iv) The η^2-acyl-isocyanide complexes {Mo}(η^2-C(O)R)(CNR') ({Mo} = $Mo(H_2B(pz^*)_2)(CO)(PMe_3)$) undergo irreversible thermal isomerization to the corresponding η^2-iminoacyl-carbonyl derivatives {Mo}(η^2-C(NR')R)(CO). This isomerization reaction follows first-order kinetics.

Keywords: Molybdenum; Acyl complexes; Structure; Reactivity

1. Introduction

The insertion of carbon monoxide into a transition metal–carbon bond is a very important transformation which finds many practical applications. Indeed, a number of catalytic carbonylations are used in both laboratory and industrial synthesis [1]. This insertion reaction converts a metal-alkyl into the corresponding metal-acyl, for which three different coordination modes are known in mononuclear species. Structures **I–III** have been authenticated by X-ray crystallography but while there are many examples of η^1- and η^2-acyls, the only agostic acyls (structure **III**) known are some molybdenum complexes of composition $[\overline{Mo(C(O)R}](X\text{–}X)(CO)(PMe_3)_2]$ (X–X = monoanionic, chelating S-ligand) prepared by our group [2,3].

Our first contribution to M-acyl chemistry (M = Mo or W) appeared in 1983 [2a] and dealt with the formation and structural characterization of various η^2-acyl complexes of molybdenum. Included in this work was also the formation of $[\overline{Mo\{C(O)Me\}}(S_2NMe_2)(CO)(PMe_3)_2]$ (**1a**), for which spectroscopy and X-ray studies revealed an unprecedented agostic acyl structure [2a]. Subsequent work, this time concerned with the tungsten system analogue, did not provide related agostic acyls but led instead to the observation of alkyl(carbonyl) and η^2-acyl structures [4]. The influence of the steric and electronic effects on the relative stabilities of these isomeric formulations was ascertained by using different alkyl groups (Me, CH_2SiMe_3, CH_2CMe_3 and CH_2CMe_2Ph) and auxiliary anionic coligands (halides, xanthates $ROCS_2^-$ and dithiocarbamates $R_2NCS_2^-$). It was found that in series of analogous complexes the η^2-acyl structure W(η^2-C(O)R) was favoured over the alkyl-(carbonyl) W(R)CO for the more sterically demanding R groups, whereas the use of strongly electron-releasing ancillary ligands (e.g. $ROCS_2^-$ and $R_2NCS_2^-$) encouraged the formation of the alkyl(carbonyl) complexes [4].

More recent work has attempted to determine the structural peculiarities of the agostic acyl structure

* Corresponding author.

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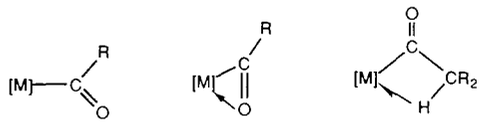


I II III

$\overline{MoC(O)CH_2}R$ (R = H or $SiMe_3$) [2d,3] and to uncover the characteristic chemical reactivity of the M-η^2-acyl linkage (M = Mo or W). In this account we summarize our work in this area concentrating specifically on the following topics: (i) the Mo–agostic acyl structure; (ii) the chemical reactivity of coordinated η^2-acyl ligand and (iii) the conversion of an η^2-acyl into an η^2-iminoacyl function by reaction with an isocyanide.

2. The molybdenum–agostic acetyl linkage, $\overline{Mo(C(O)Me)}$

The agostic acetyl **1a** was first prepared in the course of the unexpected reaction

$$[Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}Cl(CO)(PMe_3)_3] \xrightarrow{NaS_2CNMe_2} [\overline{Mo\{C(O)Me\}}(S_2CNMe_2)(CO)(PMe_3)_2] \quad (1)$$

1a

Whereas chloride replacement and either neutral ligand substitution (CO or PMe_3) or η^2- to η^1 change in the coordination of the acyl was expected, a more complex reaction ensued, causing C–Si bond heterolysis by adventitious water and formation of the agostic acetyl **1a** [2a]. Related derivatives with other dithiocarbamates **1** or xanthate: $[\overline{MoC(O)Me}(S_2COR)(CO)(PMe_3)_2]$ (**2**) have been obtained subsequently [2c,d]. In addition, the $CF_3CH_2OCS_2^-$ group has furnished a phosphonium-xanthate complex $[\overline{Mo\{C(O)Me\}}\{S_2C(PMe_3)OCH_2CF_3\}(CO)(PMe_3)_2]$ (**3**).

Three agostic acetyl complexes of Mo containing the S_2CNMe_2 (**1a**), $S_2CNC_5H_{10}$ (**1b**) and $S_2C(PMe_3)OCH_2CF_3$ (**3**) chelating ligands have been fully characterized by X-ray crystallography. A comparison of the bonding parameters within the $\overline{Mo(C(O)Me)}$ linkage of these complexes (structure **IV**) indicates that the strength of the agostic interaction decreases in the order **1a** > **1b** > **3**. For example, this is shown by the Mo–CH_3 separations of 2.60 Å, 2.66 Å and 2.76 Å, for **1a**, **1b** and **3** respectively. Similarly, the Mo–C–O angle decreases in the same order (149.2°, 147.5° and 144.5° respectively). From these data the conclusion may be drawn that the $\overline{Mo–C(O)Me}$ agostic interaction strengthens with increasing electron-releasing properties of the chelating S ligand (vide infra).

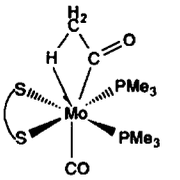
All the agostic acyls investigated display a carbonyl IR absorption in the region 1615–1580 cm^{-1}, distinctly in higher energy than in the related η^2-acyls (about 1550–1425 cm^{-1}) [2,4]. In addition, the $\overline{Mo–C(O)Me}$ protons resonate at relatively high field (δ = 1.5–2.1 ppm) and appear as a triplet owing to coupling to the two equivalent ^{31}P nuclei ($J_{HP} \approx 2$ Hz). In comparison, in the related η^2-acyls this signal appears as a singlet at lower fields (δ = 2.4–2.8 ppm). $^{13}C\{^1H\}$ NMR data for the agostic acetyls also show significant differences from those of the analogous derivatives that contain a dihapto acetyl unit.

An important characteristic of the agostic acetyls is the dynamic behavior that they exhibit in solution. Since these dynamic properties have been analyzed at length [2c,d], further discussion is not warranted here. It should be noted, however, that the results of this study clearly show that in these complexes there are small energy differences among the alkyl(carbonyl). η^2-acyl and agostic acyl structures and that, as a result, equilibria involving these species are established in solution.

It is appropriate to consider at this stage the characteristics of the Mo–acyl bond in the acyl complexes that we have prepared since we began our work. Two types of derivative can be considered.

2.1. Compounds which exhibit agostic interaction

Here we can distinguish between (a) compounds for which only the agostic structure is detected and (b) complexes with agostic structure in the solid state but that exist in solution in equilibrium with other isomeric formulations. The first of these two groups contains complexes of composition $[\overline{Mo\{C(O)Me\}}(X–X)(CO)(PMe_3)_2]$ where X–X is a dithiocarbamate R_2NCS_2 (R = Me, ^{i}Pr or C_5H_{10}) or a phosphonium xanthate $RO(PMe_3)CS_2$ (R = Me or CF_3CH_2). They display a characteristic fluxional behaviour in solution involving equilibration of the two carbonyl functions, presumably through the intermediacy of an (undetected) alkyl(carbonyl). The three xanthate derivatives $[\overline{Mo(C(O)Me)}(S_2COR)(CO)(PMe_3)_2]$(R = Me, Et or ^{i}Pr) belong to the second group. In this case, the agostic and the η^2-acyl formulations are predominant at low temperatures, and above −40°C the involvement of the alkyl(carbonyl) isomer is implied from variable-temperature IR and NMR studies.



IV

2.2. Dihapto acyl complexes

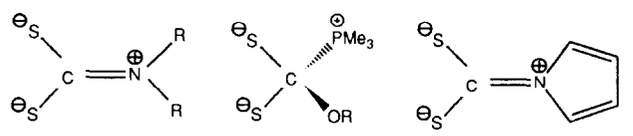
This group is the largest by far and includes compounds of composition $[Mo\{\eta^2\text{-}C(O)R\}X(CO)_n(PMe_3)_{4-n}]$ ($n = 0$–2; X = halide or pseudohalide) as well as the dihydrobis(pyrazolate) (represented by Bp′) derivatives $[Bp'Mo\{\eta^2\text{-}C(O)R\}(CO)(PMe_3)_2]$. Also included here are the pyrrol-derived dithiocarbamate complex $[Mo\{\eta^2\text{-}C(O)Me\}(S_2CNC_4H_4)(CO)(PMe_3)_2]$ and some dithiocarbamate and xanthate complexes of composition $[Mo\{\eta^2\text{-}C(O)Me\}(X\text{–}X)(CO)_2(PMe_3)]$ that result from CO replacement of one of the PMe_3 in complexes of types **1** and **2**.

The above findings together suggest that the stabilization of the agostic acyl linkage, which in these complexes is always *tran* to the CO ligand, requires the presence in the equatorial plane of a combination of a strongly chelating and electron-releasing S donors ($\sigma + \pi$) together with two (also strongly basic) PR_3 groups. Note (i) that because of the larger contribution of resonance form **V**, the dithiocarbamates are stronger donors than the xanthates, (ii) that, for similar reasons (structure **VI**), $RO(Me_3P)CS_2$ are also better donors than the xanthates, and (iii) that, owing to the loss of aromaticity of the pyrrolyl moiety implied by structure **VII**, the pyrrol-derived dithiocarbamate $C_4H_4NCS_2$ is a poorer donor than other common dithiocarbamates.

Fine tuning of the metal basicity to such a degree that stabilization of the agostic structure becomes feasible cannot be accomplished in a fully predictable manner. A clear reminder of this is the fact, already mentioned, that in the tungsten system analogue only the alkyl(carbonyl) and the dihapto acyl structures can be detected. An additional factor that cannot be underestimated is the influence on this stabilization of the different ligand stereochemistries in related complexes that exhibit the isomeric alkyl(carbonyl), dihapto and agostic acyl structures.

3. Reactivity of the coordinated acyl ligand

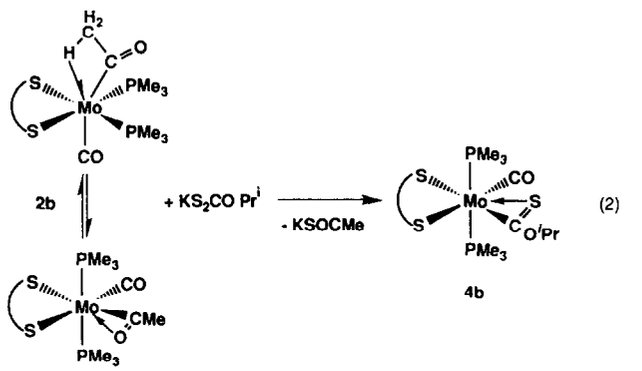
The chemical transformations of ligands constitute an important area of research in organometallic chemistry. Although earlier investigations of the acyl function have focused mainly on synthetic and structural aspects, the need to understand the intermediary role played by transition metal acyls in many laboratory and industrial transformations has motivated a number of reactivity studies [1,5]. Our interest in transition metal acyl and iminoacyl chemistry has naturally included the study of the reactivity of the acyl function. Here we wish to describe two types of reaction that take place intramolecularly and involve the η^2-acyl and another ligand.



V VI VII

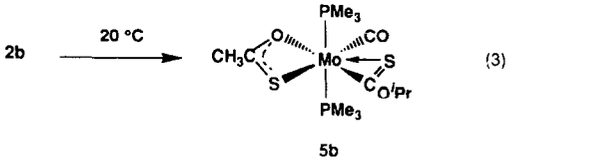
3.1. Formal insertion of sulfur into a Mo–C(O)Me bond [6]

Stirring a solution of the acyl(xanthate) complex $[Mo\{C(O)Me\}(S_2CO^iPr)CO(PMe_3)_2]$ (**2b**) under N_2 in the presence of one equivalent of the xanthate salt KS_2CO^iPr produces low yields of an alkoxythiocarbonyl derivative **4b**, as follows:



(2)

At first sight, it seems that the acyl ligand is lost during the process and also that one of the xanthate groups becomes partially desulfurized. A closer look at the reaction mixture confirms this and shows the liberation of potasium monothioacetate as a byproduct. This suggests that the reaction proceeds with loss of a sulfur atom from the coordinated xanthate in **2b** and concomitant coupling with acyl to form a monothiocarboxylate group which is then metathetically replaced by KS_2CO^iPr. Consistent with this hypothesis, a solution of the xanthate complex **2b**, when stirred at room temperature over 1–2 days, yields the monothioacetate complex **5b**, which contains a partially desulfurated isopropyl xanthate (yields are up to 90%):



(3)

In view of the facility with which reactions (2) and (3) proceed, we attempted the preparation of complexes

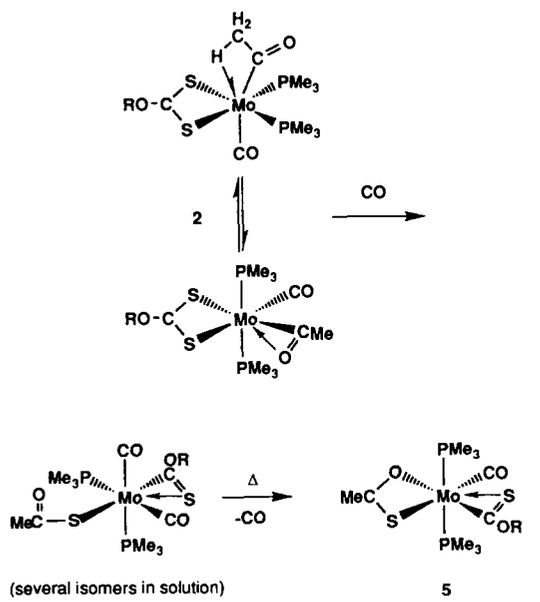
analogous to **4b**, containing related ligands, in a one-pot conversion starting from the chloro(acyl) [Mo{η^2-C(O)R}Cl(CO)(PMe_3)$_3$]. This synthetic methodology, represented as follows for the preparation of the ^{t}Bu derivative **4c**, provides moderate overall yields of these complexes (about 40%):

[Mo{η^2-C(O)Me}Cl(CO)(PMe_3)$_3$]

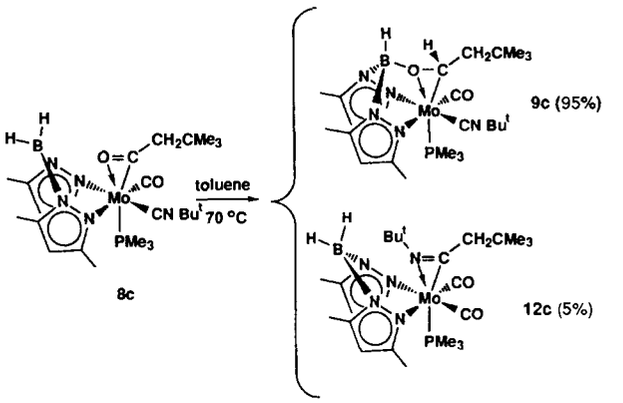
$$\xrightarrow[-KSOCMe]{2\ KS_2CO^tBu} [Mo(S_2CO^tBu)\{\eta^2\text{-}C(S)O^tBu\}(CO)(PMe_3)_2]$$
4c (4)

Spectroscopic evidence is in accord with the proposed formulation (**VIII**). The alkoxythiocarbonyl gives rise to a strong IR absorption at about 1270 cm^{-1}, close to the value of 1290 cm^{-1} found for the structurally characterized iron complex [Fe{η^2-C(S)OMe}(CO)-{P(OMe)$_3$}{$Ph_2PCH{=}C(^tBu)S$}] [7]. Moreover, the alkoxythiocarbonyl carbon directly bonded to the Mo gives rise to a triplet ($^2J_{CP} \approx 20$ Hz) in the region 290–300 ppm in the $^{13}C\{^1H\}$ spectra. The very low field chemical shift found for this signal suggests considerable carbenoid character (resonance structure **X**), which is also supported by the relatively short Mo–C(S)OR separation of 2.018(3) Å found in **4c**. The structure of this compound shows that, whilst the S atom of the η^2-C(S)O^{t}Bu ligand is in the equatorial plane (formed also by the xanthate sulfur atoms and the carbonyl carbon atom), the Mo-bound C atom of this ligand is slightly raised above this plane so that the structural features of the η^2-C(S)OR fragment become reminiscent of those of the related η^2-C(O)R ligand.

When the acetyl complexes **2** react with CO under appropriate conditions, the monocarbonyl derivatives [Mo(SOCMe){η^2-C(S)OR}(CO)(PMe_3)$_2$] (**5**) are obtained. A similar reaction takes place with the dmpe species [Mo{η^2-C(O)Me}(S_2COR)(CO)(dmpe)] (dmpe = $Me_2PCH_2CH_2PMe_2$), which yields analogous alkoxy(thiocarbonyl) complexes [Mo(SOCMe){η^2-C(S)-OR}(CO)(dmpe)] (**6**). As shown in Scheme 1, this transformation proceeds with formation of the dicarbonyl [Mo{η^1-S(O)CMe}{η^2-C(S)OR}(CO)$_2$(PMe_3)$_2$] which then undergoes loss of CO, probably induced by an η^1-to-η^2 change of the monothiocarboxylate ligand.



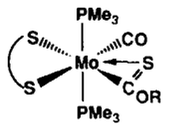
Scheme 1.



Scheme 2.

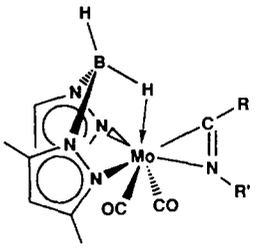
3.2. Acyl reduction by a coordinated dihydrobis(pyrazolyl)borate ligand

During the course of the studies to be described in the following section of the transformation, [Mo]{η^2-C(O)R}(CNR') → [Mo]{η^2-C(NR')R}(CO) we studied η^2-acyl complexes of composition [Bp'Mo{η^2-C(O)R}-(CO)(CN^{t}Bu)(PMe_3)][Bp' = $H_2B(pz)_2$; pz = $C_3H_3N_2$ or Bp(**7**)) (Bp' = $H_2B(pz^*)_2$; pz* = 3,5-$Me_2C_3HN_2$ or Bp* (**8**)) (R = Me (**a**), CH_2SiMe_3 (**b**) an CH_2CMe_3 (**c**)) (for the Bp system only **7c** can be isolated) and found that the Bp*–neopentyl derivative **8c** undergoes an unexpected thermal rearrangement that leads to **9c** as the major product (Scheme 2), together with minor quantities of the isomeric [Bp*Mo{η^2-C(N^{t}Bu)-CH_2CMe_3}(CO)$_2$(PMe_3)] (**12c**). Formally, **9c** results from the addition of one of the B–H bonds of the coordinated Bp* ligand to the acyl > C=O bond [8]. The reduction of a ligand is a key step in some processes that involve the hydrogenation of carbon monoxide [1]. Early studies achieved intermolecular hydrogen transfer from transition metal hydrides to coordinated acyl ligands [9] and similar acyl reductions by hydrogen, hydrosilanes and other reductants have been investigated [10]. To our knowledge, the transformation depicted in Scheme 2 is unprecedented [8]. Reactions involving the analogous derivatives of the less bulky Bp ligand **7**, as well as the Bp* complexes of the smaller Me and CH_2SiMe_3 alkyl groups **8a** and **8b**, respectively yield mostly, or exclusively, the (η^2-imino-



VIII

IX X

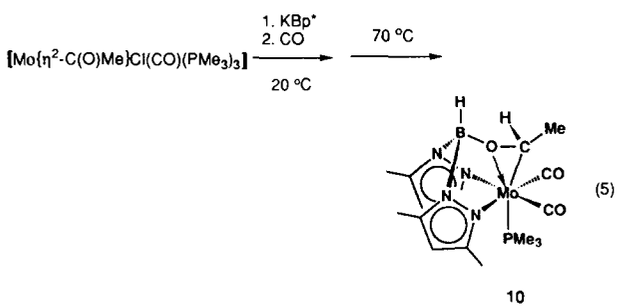


XI

13a: R = CH_3, R' = ^tBu
13b: R = CH_2SiMe_3, R' = ^tBu
13c: R = CH_2SiMe_3, R' = Xy
13d: R = CH_2CMe_3, R' = Xy

acyl)(carbonyl)isomers **11** and **12**. It is therefore clear that two competitive pathways, namely hydroboration and acyl-to-iminoacyl conversion, are available for these compounds and that the former becomes the more favorable only for the most sterically demanding combination of the Bp′ and R groups, e.g. Bp* and CH_2CMe_3.

An obvious way of avoiding the formation of the iminoacyls consists of the use of complexes that do not contain CNR ligands. Heating at 70°C a toluene solution of the dicarbonyl [Bp*Mo{η^2-C(O)Me}$(CO)_2$-(PMe_3)] prepared by the stepwise reaction of [Mo{η^2-C(O)Me}Cl$(CO)(PMe_3)_3$] with KBp* and CO provides **10**:



10 (5)

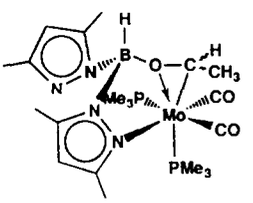
NMR data for **10** are consistent with the proposed structure which has been unequivocally established by X-ray crystallography [8]. The reactions described are highly stereospecific and provide a single stereomer as the kinetic product of the hydroboration. Longer reaction times also give other isomers whose nature is under investigation.

The η^2-iminoacyl ligand of the related complexes, [Bp′Mo{η^2-C(N^{t}Bu)R}$(CO)_2(PMe_3)$] (Bp′ = Bp (**11**) or Bp* (**12**)) can also be hydroborated, although, in general, more extreme conditions are needed [8]. In some cases, in addition to the hydrogenated products, compounds that contain a non-clasical B–H–Mo interaction are also formed. The following complexes **13a–13d** (structure **XI**) exhibiting such an interaction have been isolated and their structures ascertained by spectroscopy. That of **13a** has been confirmed by X-ray crystallography [3]. All attempts to convert these compounds into the corresponding hydroboration products have proved fruitless. Hence they do not seem to be directly involved in the hydroboration and therefore the intermediacy in this process of an M–H complex appears unlikely.

Kinetic studies on the transformation depicted in Scheme 2 show it to be intramolecular. Its course can be monitored by $^{31}P\{^1H\}$ NMR spectroscopy. First-order behavior has been ascertained over at least three to four half-lives. A comparative kinetic study of the conversion of **8c** into **9c** and of that of the analogous species containing deuterated $D_2B(pz^*)_2$ afforded rate constants that were identical within experimental error (70°C; $k_{obs} = 1.073(3) \times 10^{-3}$ s^{-1}) [3]. Therefore the rate-determining step does not involve B–H rupture. Dissociation of one of the pyrazolyl arms (pz^*) of the Bp* could allow the close approach of the B–H and C=O functions needed for the reaction to take place. This seems to be in accord with the already-mentioned fact that in analogous complexes, e.g. of types **7** or **8**, the reaction becomes more facile when the steric demands of the Bp′ and R groups increase. Additional support comes from the isolation of the complex [H(pz^*)B(pz^*)Mo{HC(O)Me}$(CO)_2(PMe_3)$] (**14**) (structure **XII**), during the hydroboration of [Bp*Mo-{η^2-C(O)Me}$(CO)_2(PMe_3)$] in the presence of three to five equivalents of PMe_3 [8]. A definite and more precise proposal is nonetheless delayed until the results of the more detailed kinetic and mechanistic studies at present under way, become available.

3.3. The [Mo]{η^2-C(O)R}(CNR′) to [Mo]{η^2-C(NR′)R}-(CO) isomerization

Organic isocyanides CNR are pseudo-isoelectronic with CO and exhibit similar bonding capabilities. Both

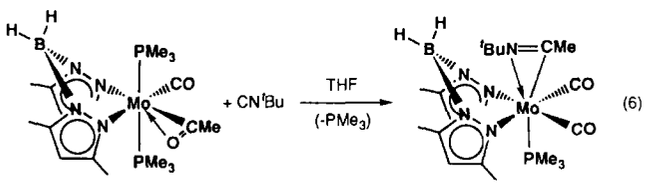


XII

Scheme 3.

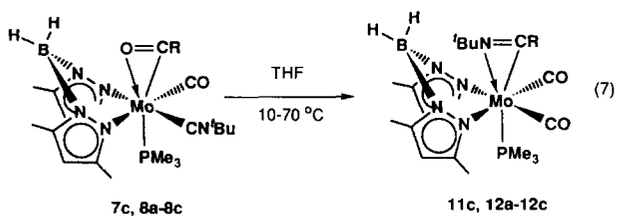
types of molecule participate extensively in insertion reactions into M–C bonds. Competition reactions involving CO and CNR are expected to lead preferentially to the iminoacyl products, and indeed a number of cases in the literature confirms this. In other instances, however, either the acyl, or a mixture of the acyl and iminoacyl products, has been obtained [11]. A survey of the literature on these reactions suggests that the iminoacyls are the thermodynamic products and consequently that CO insertion may be imposed on kinetic grounds. Despite this, the isomerization represented in Scheme 3 has never been demonstrated. As mentioned in the previous section, **8c** rearranges thermally to the hydroboration product **9c**, but small amounts of a second species, identified as the η^2-iminoacyl(carbonyl) isomer $[Bp^* Mo\{\eta^2\text{-}C(N^tBu)CH_2CMe_3\}(CO)_2(PMe_3)]$ (**12c**) are also produced. The study of this and other related transformation demonstrates the thermodynamic preference for the iminoacyl(carbonyls).

The complex $[BpMo\{\eta^2\text{-}C(O)Me\}(CO)(PMe_3)_2]$ reacts rapidly with one equivalent of CN^tBu to yield **11a**;



(6)

where THF = tetrahydrofuran. However, the lability of the supposed η^2-acyl(isocyanide) intermediate, $[BpMo\{\eta^2\text{-}C(O)Me\}(CO)(CN^tBu)(PMe_3)]$ (**7a**) prevents observation of the desired transformation (Scheme 3). Notwithstanding, compounds of this type, e.g. **7c** and **8a–8c** can be isolated for more sterically demanding combinations of the Bp′ and R groups and then isomerized thermally to the final η^2-iminoacyl(carbonyl) products;



(7)

7c, 8a-8c 11c, 12a-12c

A comparative study of the rate of isomerization shows that it increases in the order CH_2CMe_3 < CH_2SiMe_3 < Me and Bp* < Bp. Kinetic measurements indicate clean first-order kinetics over three to four half-lives. Fig. 1 shows a representation of $\ln(C/C_0)$ as a function of time for the complex $[BpMo\{\eta^2\text{-}C(O)CH_2CMe_3\}(CN^tBu)(CO)(PMe_3)]$ (**7c**). From the rates determined at four different temperatures in the range 42–66°C, $\Delta H^{\#}$ and $\Delta S^{\#}$ values of 20.3 ± 1.4 kcal mol^{-1} and -12.6 ± 1.2 cal mol^{-1} K^{-1} respectively have been computed (Fig. 2). The available data are in accord with deinsertion as the rate-determining step (to yield a sterically congested seven-coordinated alkyl(carbonyl)(isocyanide) intermediate), followed by fast irreversible rearrangement to the η^2-iminoacyl(carbonyl) product. With this assumption, the rate of the reaction should not be greatly sensitive to the nature of the migrating isocyanide ligand. This is in fact the case, since the rate constants for the isomerization of the complexes $[Bp^* Mo\{\eta^2\text{-}C(O)CH_2SiMe_3\}(CO)(CNR')(PMe_3)]$ [13], that contain CNR′ groups with different insertion capabilities [14], differ by only one order of magnitude (24°C; $k_{obs} = 1.6 \times 10^{-3}$ s^{-1} for CN^tBu; $k_{obs} = 1.6 \times 10^{-2}$ s^{-1} for CNC_6H_3-2,6-Me_2).

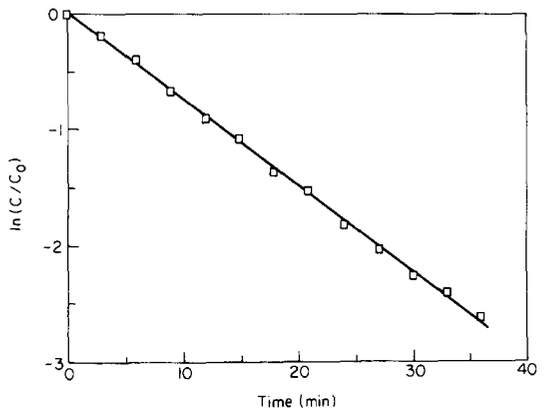


Fig. 1. Plot of $\ln(C/C_0)$ as a function of time for the thermal conversion (66°C) of **8c** into **12c**.

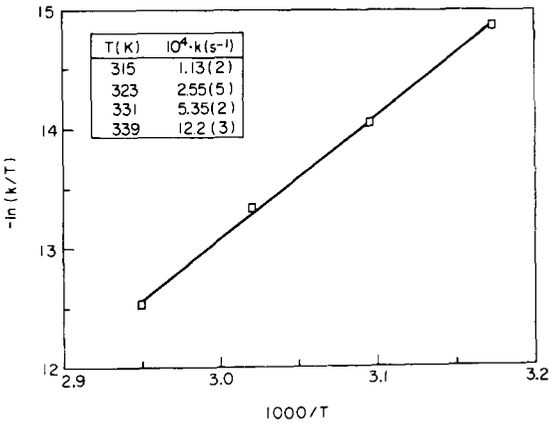


Fig. 2. Plot of $\ln(k/T)$ vs. $1000/T$ for the thermal conversion of **8c** into **12c** in toluene at four temperatures between 42 and 66°C.

Although these conclusions regarding the thermodynamic preference for the isocyanide insertion over the analogous CO insertion reaction apply strictly to the complexes investigated, they may have broader general applicability. The formation of acyl derivatives under conditions in which the alkyl group could also migrate to a CNR site may therefore be kinetically driven. If this is the case, irreversible isomerization of these known acyl(isocyanides) should be feasible and it might be accomplished under appropriate conditions.

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References and note

[1] (a) F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988; (b) J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987; (c) H. Werner, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1077; (d) A. Wojcicki, *Adv. Organomet. Chem., 11* (1973) 88; (e) F. Calderazzo, *Angew. Chem., Int. Ed. Engl., 16* (1977) 299; (f) E.J. Kuhlmann and J.J. Alexander, *Coord. Chem. Rev., 33* (1980) 195; (g) J.J. Alexander, in F.R. Hartley and S. Patai (eds.), *The Chemistry of the Metal–Carbon Bond*, Vol. 2, Wiley, New York, 1985, Chapter 5; (h) L.D. Durfee and I.P. Rothwell, *Chem. Rev., 88* (1988) 1059; (i) P.M. Treichel, *Adv. Organomet. Chem., 11* (1973) 21; (j) E. Singleton and H.E. Oosthuizen, *Adv. Organomet. Chem., 22* (1983) 209; (k) P.S. Braterman, *Reactions of Coordinated Ligands*, Plenum, New York, 1986.

[2] (a) E. Carmona, L.J. Sánchez, M.L. Poveda, J.M. Marin, J.L. Atwood and R.D. Rogers, *J. Chem. Soc., Chem. Commun.*, (1983), 161; (b) E. Carmona, L.J. Sánchez, J.M. Marín, M.L. Poveda, J.L. Atwood, R.D. Riester and R.D. Rogers, *J. Am. Chem. Soc., 106* (1984) 3214; (c) E. Carmona, L. Contreras, M.L. Poveda and L.J. Sánchez, *J. Am. Chem. Soc., 113* (1991) 4322; (d) L. Contreras, A. Monge, A. Pizzano, C. Ruíz, L. Sánchez and E. Carmona, *Organometallics, 11* (1992) 3971.

[3] L. Contreras, A. Pizzano, L.J. Sánchez and E. Carmona, submitted for publication.

[4] (a) E. Carmona, L. Contreras, M.L. Poveda, L.J. Sánchez, J.L. Atwood and R.D. Rogers, *Organometallics, 10* (1991) 61; (b) E. Carmona, L. Contreras, E. Gutiérrez-Puebla, A. Monge and L.J. Sánchez, *Organometallics, 10* (1991) 71.

[5] (a) M. Brookhart, F.C. Rix, J.M. DeSimone and J.C. Barborak, *J. Am. Chem. Soc., 114* (1992) 5894; (b) J.B. Sheridan, J.R. Johnson, B.M. Handwerker and G.L. Geoffroy, *Organometallics, 9* (1990) 66; (c) H. Adams, N.A. Bailey, C.E. Tattershall and M.J. Winter, *J. Chem. Soc., Chem. Commun.*, (1991) 912; (d) I.H. Hart, J.C. Jeffery, R.M. Lowry and F.G.A. Stone, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1703.

[6] L. Contreras, A. Pizzano, L. Sánchez, E. Carmona, A. Monge and C. Ruiz, *Organometallics, 14* (1995) 589.

[7] (a) P. Robert, H. Le Bozec, P.H. Dixneuf, F. Hartsock, N.J. Taylor and A.J. Carty, *Organometallics, 1* (1982) 1148; (b) A. Samb, B. Demerseman, P.H. Dixneuf and C. Mealli, *Organometallics, 7* (1988) 26.

[8] A. Pizzano, L. Sánchez, E. Gutiérrez, A. Monge and E. Carmona. *Organometallics, 14* (1995) 14.

[9] (a) G. Erker, K. Kropp, C. Kruger and A.-P. Chiang, *Chem Ber., 115* (1982) 2447; (b) B.D. Martin, K.E. Warner and J.R. Norton, *J. Am. Chem. Soc., 108* (1986) 33; (c) J.A. Marsella, K. Folting, J.C. Huffman and K.G. Caulton, *J. Am. Chem. Soc., 103* (1981) 5596; (d) E.A. Maatta and T.J. Marks, *J. Am. Chem. Soc., 103* (1981) 3576.

[10] B.T. Gregg and A.R. Cutler, *Organometallics, 11* (1992) 4276; (b) I. Kovacs, A. Sisak, F. Ungvary and L. Marko, *Organometallics, 7* (1988) 1025; (c) R.W. Wegman, *Organometallics, 5* (1986) 707; (d) M. Akita, O. Mitani, M. Sayama and Y. Morooka, *Organometallics, 10* (1991) 1394; (e) J.C. Selover, G.P. Vaughn, C.E. Strouse and J.A. Gladysz, *J. Am. Chem. Soc., 108* (1986) 1455.

[11] For leading references on these topics see [12].

[12] A. Pizzano, L. Sánchez, M. Altmann, A. Monge, C. Ruiz and E. Carmona, *J. Am. Chem. Soc., 117* (1995) 1759.

[13] M.M. Conejo, A. Pizzano, L. Sánchez and E. Carmona, manuscript in preparation.

[14] P.P.M. Lange, H.-W Früauf, M.J.A. Kraakman, M. Wijnkoop, M. Kranemburg, A.H.J.P. Groot, K. Vrieze, J. Fraanje, Y. Wang and M. Numan, *Organometallics, 12* (1993) 417.